Cha, Choi, and Park Reply: We suggested that flavors of density functional theory (DFT) lead to unrealistic stabilization of the bonded state of four hydrogen molecules onto the Ca cation center, in contrast to the results of correlated wave function theories [1]. Ohk *et al.* [2] commented pertinently that a larger basis set should have been used to obtain the converged results of correlated theories. Even with the elaborated calculations, the $Ca^{1+}4H_2$ system constitutes an extraordinary example for which gradient-corrected density functionals (GGAs) lead to overbinding results. The same feature persists in charge neutral $Ca4H_2$ system, as shown in Fig. 1. Here, BLYP and PBE denote the GGA functionals [3–5]. Such GGA overbinding should be due to the failure of these particular functionals in the description of wave function symmetry change: the highest occupied molecular orbital (HOMO) drastically changes from $4s$ to $3d_{xy}$ upon $4H_2$ adsorption [1]. Koch *et al.* discussed that similar DFT behaviors can be traced to the overestimation of exchange energy upon the $s \rightarrow d$ transfer [6].

The question arises whether the aforementioned $s \rightarrow d$ transfer takes place in more realistic systems. According to our calculations [7], when a Ca atom is placed onto aromatic planes, one of the Ca's $4s$ electrons is transferred to the bonding πd orbital which is delocalized over the surface π network, while the other one remains in the singly occupied $4s$ orbital, yielding a triplet ground state. Upon adsorption of $4H_2$, the separated two electrons tend to recombine in the Ca's $3d_{xy}$ orbital, making a singlet ground state. For an explicit comparison, we calculated the energy of the singlet ground state of the $4H_2$-adsorbed Ca-coronene with respect to the triplet ground state of the Ca-coronene system and separated four H_2 molecules. The MP2 and PBE results are found to be -0.19 and -0.66 eV, respectively [8]. This clearly indicates that the GGA overbinding also occurs in the model systems of Ca-adsorbed graphenes.

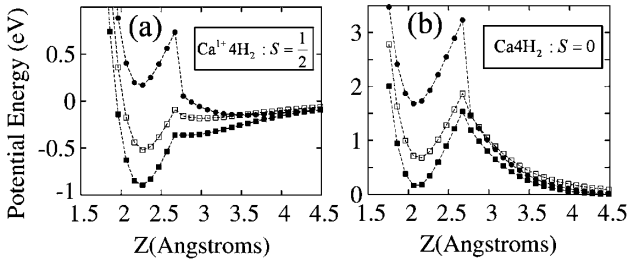

FIG. 1. The potential energy curve for (a) $Ca^{1+}4H_2$ and (b) $Ca4H_2$. The geometry and reaction coordinates are explained in Ref. [1]. Solid circles, open squares, and solid squares were calculated with MP2, BLYP, and PBE, respectively. The cc-pVQZ basis set was employed with the counterpoise correction. The insets indicate the molecular spin state.

However, when a Ca atom adsorbs onto small aromatic molecules (e.g., benzene, anthracene, or naphthacene), the system develops a stable doubly occupied πd orbital even before $4H_2$ adsorption, yielding a singlet ground state [9]. As such, the chance of the adsorption-induced $s \rightarrow d$ transfer is effectively eliminated. For those systems, common DFT functionals can be better trusted, and the Sun *et al.*'s comparison of MP2 and PBE is noteworthy[9]. For the detailed understanding of the $s \rightarrow d$ transfer phenomenon and the related GGA overbiding problem, a more intensive study needs to be performed with various substrate conditions.

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